

Colour Changes of Pine and Fir Wood Treated with Several Titanium and Zinc-Oxide Based Nanocompounds

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Abstract

In this work, the colour changes of pine and fir wood treated with several nano-compounds were investigated. Surface treatments with titanium- and zinc- oxide based nanocompounds clearly retarded lightness reduction to a certain extent in both pine and fir wood tested. The maximum lightness improvement was obtained with the nano-compound B (titanium oxide based; *rutile*), which was improved by 57.8% for fir and 44.8% for pine wood, respectively. On the other hand, the treated samples showed the least redness (Δa^*) and yellowness (Δb^*) reduction in both wood species. Moreover, the same compound was considerably more effective in reducing the rate of lightness decrease in fir wood, whereas compound A (titanium oxide based; 75% *anatase*, 25% *rutile*) was more effective in reducing the rate of lightness decrease in pine wood against ultraviolet irradiation. The highest lightness improvement occurred in fir (47.9%) with compound B, while the highest lightness improvement took place in pinewood (56.5%) with compound A. In addition, the marked effect of whiteness and yellowing colour protection with the nanocompound based coatings tested against natural and UV irradiation weathering was shown in the work. The surface coating agents typically resulted in a colour reduction improvement (ΔE) of 12.2 value units for naturally weathered fir wood, and of 10.3 value units for UV irradiated fir wood. It was shown that nanocompound B was considerably more effective in reducing the rate of total colour decrease in fir wood both in natural weathering and artificial UV-chamber weathering.

Keywords

Wood; Zinc Oxide; Titanium Oxide; Nanocompounds; Natural Weathering; Artificial UV-Chamber Weathering

Introduction

Wood has been being used from the dawn of civilization for numerous purposes. Humans have come to depend upon it in many ways; wood is a raw material in the manufacture of lumber, furniture, paper and other wood based products. In fact, wood is a fibrous and organic material which is composed of cellulose fibers embedded in a matrix of lignin and hemicelluloses. Moreover, wood can not be only considered for its fibrous structure or physical properties, but also for its aesthetic aspects (Janin *et al.* 2001).

Wood with its particular grain exhibits its aesthetic and natural chromatic appearance; this is created by deposits of some chemicals (i.e. extractives) in the cell lumen and grain pattern (Fengel and Wegener 1984). For specific structures, it plays an important role during selection due to its pleasant pattern and colour. Hence, if someone considers how attractive wood has become for costumers today one should take into consideration of its natural appearance. This may be the most important criterion at the moment of using it in several applications.

When wood is exposed to sun, its colour changes drastically. Some wood species become grey in colour, others turn yellow, orange, red or even dark-brown depending upon the influence of the wood constituents especially the extractives (Sandermann and Schlumbom 1962). However, it is well known that the chromatic changes of wood after exposure to ultraviolet (UV) radiation can produce aesthetical damages particularly in light-coloured species. A number of scientists have reported that the UV light is one of the most critical factors contributing to the

weathering of wood (Hon *et al.* 1980, Hon and Feist 1981, Feist and Hon 1984, Cassens and Feist 1991; Sahin and Mantanis 2011a).

Hon (1981) has proposed that wood is capable of absorbing all wavelengths of electromagnetic radiation so as to initiate photochemical reactions that can eventually lead to wood discolouration and photodegradation. However, the appearance of wood in many applications is very important the moment of using it. Therefore, the stability of colour to sun exposure is an essential issue. As a result of technological developments, there have been developed new agents and techniques applicable to the wood surfaces for protecting its natural appearance and colour characteristics (Cassens and Feist 1991, Mc Donald *et al.* 1996, Yamamoto *et al.* 2007, Sahin and Mantanis 2011b).

Oltean *et al.* (2010) reported that colour change of wood caused by sunlight exposure in indoor applications is a major downgrading parameter that has a detrimental economical impact on high-valued wood products. Tolvaj and Mitsui (2010) found that neither xenon nor mercury lamp light can accurately simulate sunlight, but a wide range of colour changes were caused by the applied light sources. In spite of the wide colour range, a linear correlation was found between the lightness and the colour hue. Garcia *et al.* (2014) proposed that the CIELab system can be a useful technique for measuring colour changes of teak wood (*Tectona grandis*) exposed to UV radiation under accelerated aging conditions. Notwithstanding it has already been reported that the quantitative colourimetric analysis to establish wood colour is a simple procedure which describes the natural colour properties and the transformation of sensorial impressions into numbers (Janin *et al.* 2001, Pastore *et al.* 2004, Oltean *et al.* 2010, Sahin and Mantanis 2011a, Garcia *et al.* 2014). In the literature, consistently the CIE 1976 ($L^* a^* b^*$) system has been being used to interpret precisely the colour variations of wooden surfaces (Janin *et al.* 2001, Pastore *et al.* 2004, Yamamoto *et al.* 2007, Tolvaj and Mitsui, 2010, Oltean *et al.* 2010, Sahin and Mantanis 2011a).

Nanotechnology is a new research area that investigates the matter on an atomic, molecular and supramolecular scale, and can be used across all the science fields like surface science, organic chemistry, molecular biology, material engineering, semiconductor physics, etc. However, although modern nanotechnology is quite new, nanoscale materials have been used for centuries. One example of this use was the alternate-sized gold and silver particles creating colours in the stained glass windows of churches that were applied hundreds of years ago. In nowadays, scientists and engineers investigate thoroughly a wide variety of ways to deliberately 'manipulate' materials at the nanoscale level to take advantage of their enhanced properties and greater chemical reactivity, as compared with their larger-scale counterparts.

The aim of the work was to evaluate the influence of nano- based surface treatments on black pine (*Pinus nigra* Arnold var. *nigra*) and Greek fir (*Abies cephalonica* Loudon) wood. The treated and untreated wood surfaces were then exposed to natural weathering as well as to artificial UV-chamber radiation, and the colour changes were measured.

Materials and Methods

Chemical formulations used in the work are shown in Table 1. Two nanocompound systems were used, namely *titanium oxide* (TiO₂) and *zinc oxide* (ZnO), in four different formulations. One formulation (A) is based on titanium oxide combining the mineral forms of *anatase* (75%) and *rutile* (25%), while another one (formulation B) is made solely by the *rutile-form* of titanium oxide. Formulation C is entirely comprised of zinc oxide and formulation D is a combined formulation of titanium oxide and zinc oxide (Table 1). The nanocompounds tested are proprietary products for the protection of wood surfaces against the UV radiation; they have been developed by the company NanoPhos S.A. (Lavrio, Greece). Two percent emulsion solutions were prepared based on the metal oxides (TiO₂, ZnO). All four nanocompounds were comprised of ~80 nm particles. Their specific size distribution is not available.

Pine and fir wood specimens were prepared and conditioned to 12% moisture content prior to experiments. Five samples cut in the form of 50x50x20 mm (tangential x radial x longitudinal) were used in each treatment. All four formulations were applied to wood samples in atmospheric conditions simply by soaking in a bath for 10 sec. After the immersion, treated samples as well as untreated (control) samples were conditioned to 12% moisture content in a conditioning room at 65% relative humidity and 20°C for two weeks. The retention of nanocompounds in the wood mass is shown in Table 2.

It was supposed in this work that irradiation having $\lambda > 280$ nm is suitable for the rapid monitoring of the UV degradation of wood. Consequently, the UV irradiation on wood samples was utilised in a UV chamber with single UVA-340 lamps. The irradiation period was 100 h in total; the specimens were exposed to the UV environment directly. The distance between the wood samples and the lamp was approximately 20 cm. The temperature within the irradiation chamber was 25°C. Furthermore, natural weathering of the wood samples was conducted in the south part of Sobu Hight (Isparta, Turkey) in order to have the maximum sunlight absorbed by the wood surfaces.

As mentioned previously, the colour changes of wood during UV irradiation or natural weathering are often assessed by the CIE $L^*a^*b^*$ colour system which determines the lightness (L^*), redness (a^*) and yellowness (b^*).

The discolouration of wood specimens treated with the nanocompounds was evaluated using a colour spectrophotometer (*X-Rite SP62 Portable Spectrophotometer*). The device was beforehand calibrated against a white and black working standard supplied with the instrument. Measurements were made using a *D65 illuminant* and a 10-degree standard observer. Three (3) measurements for each treatment of the wood species were carried out, and the average colour values were recorded.

TABLE 1 FORMULATIONS OF NANOCOMPOUNDS USED IN THE WORK (EMULSION SOLUTION 2%)

Formulation	Type of nanocompound*
A	Titanium oxide (75% anatase, 25% rutile)
B	Titanium oxide (100% rutile)
C	Zinc oxide
D	Combined formulation of titanium oxide and zinc oxide (50% of B + 50% of C)

* Emulsion formulations used belong to the company NanoPhos S.A. (Lavrio, Greece)

TABLE 2 RETENTION OF NANOCOMPOUNDS IN THE WOOD MASS

Formulation	Species	Retention level (kg m ⁻³)	Std. deviation
A	Pine	0.36	0.06
	Fir	0.44	0.03
B	Pine	0.35	0.05
	Fir	0.45	0.02
C	Pine	0.39	0.03
	Fir	0.47	0.04
D	Pine	0.39	0.03
	Fir	0.46	0.05

Results and Discussion

Tables 3 and 4 summarise the CIE colour values of L^* , a^* and b^* for coated and control fir and pine wood after the natural and UV-chamber weathering tests, respectively. It appears that the wood species influence the discoloration properties. The lightness reduction values of (ΔL) -22.64 and -19.35 were observed for untreated fir and pine wood under natural weathering conditions, respectively. Data of ΔL in Table 3 show that surface coating with each of the four formulations clearly retarded the ΔL change in both wood species. The maximum lightness improvement attained was made with the compound B, both for fir (57.8%) and pine wood (44.8%).

Furthermore, the green-red (a^*) and blue-yellow (b^*) colour coordinates were changed significantly depending upon the treatment used. The treated wood surfaces mostly showed the least redness (Δa^*) and yellowness (Δb^*) reduction for both wood species, as shown in Table 3.

Table 4 shows the comparative colour changes with all of the nanocompound formulations against UV-chamber irradiation for both fir and pine wood. It can be seen that compound B is proved to be considerably more effective in reducing the rate of lightness decrease in fir wood; whereas, compound A was rather more effective in reducing the rate of lightness decrease in pine wood against UV. The highest lightness improvement (47.9%) took place in fir wood with compound B, while the highest lightness improvement in pine wood (56.5%) occurred with compound A. In general, it is known that the discoloration of wood is not well understood for most of the wood species (Feist and Hon 1984). To determine the causes of discolouration, one has to understand factors such as composition of

wood extractives, temperature, humidity and storage conditions (Hon *et al.* 1980, Kalnins and Knaebe 1992, McDonald *et al.* 1996).

TABLE 3 SURFACE COLOUR CHANGES IN CONTROL AND COATED WOOD SAMPLES AFTER NATURAL WEATHERING (VALUES IN METRIC)

Fir wood						
Compound	ΔL	Change (%)	Δa	Change (%)	Δb	Change (%)
Control	-22.64	0	3.46	0	-0.48	0
A	-11.14	50.7	2.68	22.5	4.18	970.1
B	-11.04	57.8	2.62	24.3	5.92	1333.3
C	-12.57	44.4	2.61	24.5	4.50	1016.6
D	-12.01	46.9	2.86	17.3	5.88	1325.0
Pine wood						
Control	-19.35	0	1.26	0	-11.65	0
A	-11.71	39.5	1.90	50.8	-0.38	96.7
B	-10.69	44.8	1.86	47.6	1.83	115.6
C	-11.91	38.4	1.91	51.6	1.38	111.9
D	-11.23	41.9	2.14	69.8	-0.16	98.6

TABLE 4 SURFACE COLOUR CHANGES IN CONTROL AND COATED WOOD SAMPLES AFTER UV-CHAMBER WEATHERING (VALUES IN METRIC)

Fir wood						
Compound	ΔL	Change (%)	Δa	Change (%)	Δb	Change (%)
Control	-5.32	0	1.80	0	12.28	0
A	-3.38	36.4	0.9	50.0	9.40	23.5
B	-2.77	47.9	0.61	66.1	8.59	30.1
C	-4.67	12.2	1.45	43.8	10.0	18.6
D	-5.06	4.9	1.30	27.8	8.83	28.1
Pine wood						
Control	-3.38	0	0.95	0	5.62	0
A	-1.47	56.5	0.25	73.7	4.69	16.5
B	-2.86	15.4	0.87	8.4	5.32	5.3
C	-2.73	19.2	0.51	46.3	4.73	15.8
D	-2.81	16.9	0.83	12.6	5.11	9.1

Yamamoto *et al.* (2007) suggested that light-coloured wood specimens (i.e., $L^* \geq 70$, $a^* < 8$) such as softwoods usually undergo photo-darkening and photo-bleaching when exposed to light in the UV chamber. Though it was supposed that there was a tendency for initial colour of wood species and their discolouration patterns: the smaller the initial L^* value was, the shorter the wavelength would be, at which the darkening/bleaching transition occurred for L^* ; the larger the initial a^* value was, the shorter the wavelength of the darkening/bleaching transition for a^* would be. There was no obvious tendency for parameter b^* (Yamamoto *et al.* 2007). Similar results were observed in this work; the wood samples under natural weathering showed lower reduction for the contribution of yellow colour Δb^* (Table 3) as compared with that of UV-chamber irradiation (as shown in Table 4).

Noticeably, the yellowness (Δb^*) reduction was greater in the UV-chamber irradiated fir wood as compared with that of pine wood.

The marked effect of surface whiteness and yellowing colour protection with the nanocompound-based coatings against natural weathering and UV-chamber irradiation is noticeable as shown in Table 5. It was showed that the changes in whiteness and yellowness values were identical to each other, for both fir and pine wood. However, the

compound A showed the highest protection effect in natural weathering as well as in UV-chamber irradiation for both pine and fir wood samples. For the whiteness and yellowness reduction under natural weathering conditions, the maximum improvement of 16.8% and 32.8% for fir wood, and of 62.4% and 52.8% for pine wood were taking place with the surface coating based on the nanocompound A.

TABLE 5 SURFACE WHITENESS (ASTM E313) AND YELLOWNESS (ASTM D1925) CHARACTERISTICS OF CONTROL AND TREATED WOOD SAMPLES

	Whiteness index		Yellowness index	
Fir wood				
	W*	UV**	W	UV
Control	10.86	16.22	21.30	22.47
A	9.03	12.20	14.90	14.24
B	10.15	11.08	17.48	14.49
C	10.00	14.35	16.16	19.64
D	10.52	12.21	18.37	16.78
Pine wood				
Control	11.60	7.71	18.37	10.95
A	4.36	5.84	8.63	7.63
B	6.65	7.15	11.34	10.11
C	6.66	6.38	11.52	8.67
D	4.47	6.88	9.03	9.71

*Note: W: Naturally weathered; **UV: UV-chamber weathered.

Similarly, the same trend was observed in the UV-chamber weathered woods; that is, the maximum improvement of whiteness and yellowness reduction of pine was found to be of 24.2% and 39.3% with the nanocompound A, respectively. In addition, the maximum yellowness improvement (36.7%) of fir wood was realised also with the titanium-oxide based compound (A) coating.

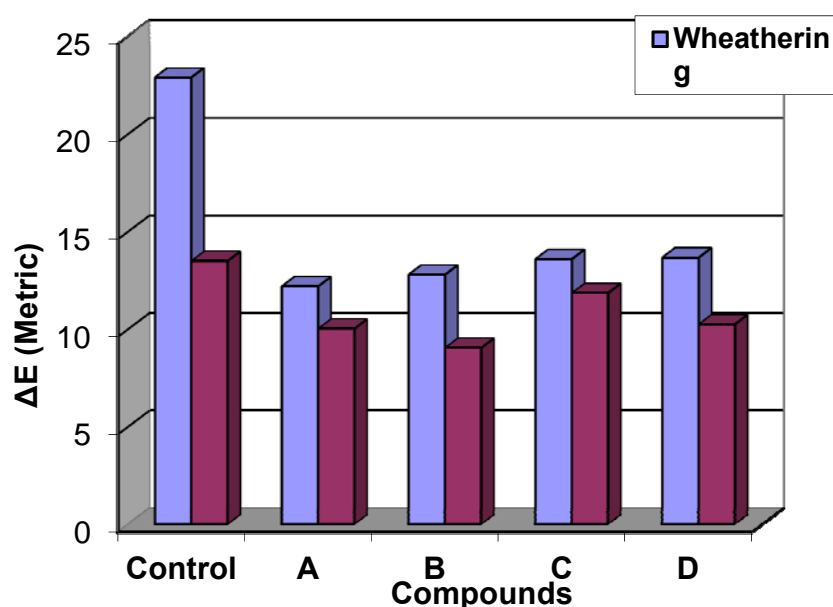


FIGURE 1 INFLUENCE OF UV IRRADIATION AND NATURAL WEATHERING ON TOTAL COLOUR DIFFERENCES (ΔE^*) IN FIR WOOD

The influence of UV-chamber and natural weathering tests on total colour differences (ΔE^*) of fir and pine species is given in Figs. 1 and 2, respectively. It was noted that the UV-light exposure of untreated pine and fir wood led at the beginning to a rapid colour change. The uncoated fir and pine total colour difference values showed a systematic downgrading trend to lower values in both the UV-chamber and the natural weathering process. However, the colour reductions were more severe for the naturally weathered surfaces of wood. The final total

colour change was approx. 22.9 and 13.5 value units in the uncoated fir wood, after natural weathering and UV irradiation, respectively (Fig. 1).

The surface treatments typically resulted in effective colour reduction improvement (ΔE) of ca. 12.2 value units for naturally weathered fir, and 10.3 value units for UV-irradiated fir; that is much less than the mere 46.8% and 23.7% improvement achieved with the natural weathering and UV irradiation, respectively. It was noted that compound B was considerably more effective in reducing the rate of total colour reduction for fir wood in both weathering tests.

For pine wood (Fig. 2), the total colour difference showed a trend that was somewhat similar to that of fir wood. As a matter of fact, the highest colour differences of ca. 22.6 and 6.6 value units occurred in uncoated pine wood at the natural and UV-chamber weathering, respectively.

It was found that the protection of wood specimens with all three coatings (A, B, C) led to lesser discolouration of pine wood at a certain extent. This observation, which is in accordance with the previous findings (Oltean *et al.* 2010, Sahin and Mantanis 2011a, Garcia *et al.* 2014) clearly shows that such surface coatings are sound in protecting the photo-discolouration of wood up to some degree. Noticeably, wood coated with the nanocompound A was largely protected against discolouration (ΔE^* = approx. 11.87 value units for natural weathering; 4.92 value units for UV-chamber irradiation weathering).

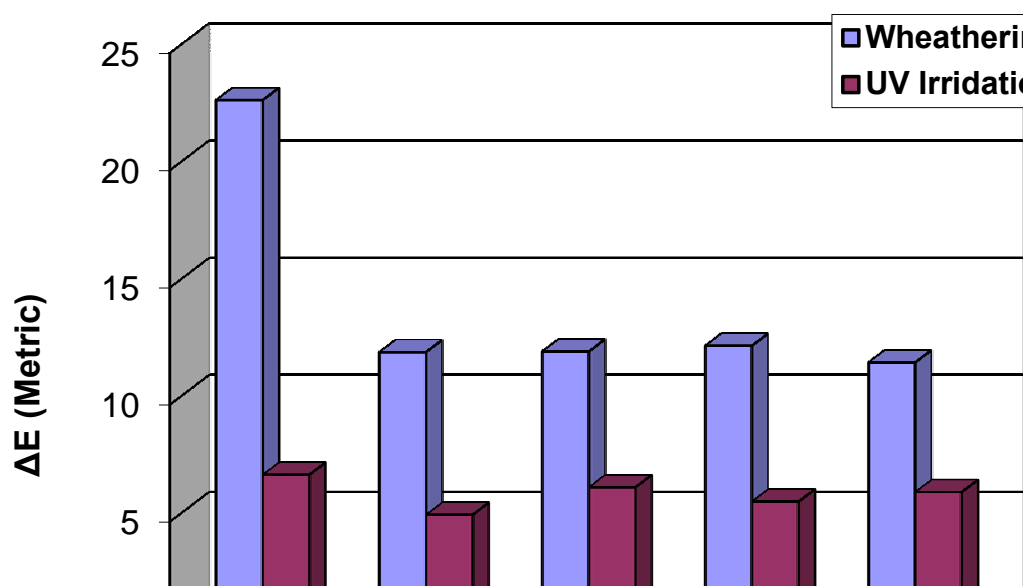


FIGURE 2 INFLUENCE OF UV IRRADIATION AND NATURAL WEATHERING ON TOTAL COLOUR DIFFERENCES (ΔE^*) IN PINE WOOD

As mentioned previously, nanotechnology deals with the very small particles that can impart enhanced properties into the materials (i.e. wood coating agents) and can create greater chemical affinity. Furthermore, in this study it has clearly been shown that anti-UV compound treatments were quite effective in inhibiting the photo-discolouration of wood. This is probably due to a very small size of nanoparticles based on metal oxides that can penetrate into the cell wall effectively altering thus its surface chemistry and resulting in a higher protection against UV radiation (Oltean *et al.* 2010, Garcia *et al.* 2014). In addition, similar results have also been reported in other works (Sahin and Mantanis 2011a, 2011b).

Conclusions

Surface coating treatments of wood with four titanium- and zinc- oxide based nano- compounds tested partly retarded the lightness reduction to a certain extent, in both black pine and fir wood. The maximum lightness improvement was obtained with a titanium-oxide based nanocompound, which was improved by 57.8% for fir and 44.8% for pine. The coated wood samples exhibited the least redness (Δa^*) and yellowness (Δb^*) reduction in both wood species. It was found that the titanium-oxide based compound was considerably more effective in reducing the rate of lightness decrease in fir wood; whereas, a titanium oxide-based nanocompound was more effective in

reducing the rate of lightness decrease in pine wood against UV irradiation. In addition, the marked effect of whiteness and yellowing colour protection with the nanocompound based coatings tested against natural as well as UV-chamber irradiation weathering was investigated in this work with some relatively positive results. In general, the zinc-oxide based nanocompounds tested were proved to be less effective than those of titanium-oxide. Finally, a distinct effect of surface whiteness and yellowing colour protection with the nano-based treatments against both natural weathering and UV-chamber irradiation was observed for fir and pine wood.

ACKNOWLEDGEMENTS

The authors would like to thank the Greek nanotech company NanoPhos S.A. (Lavrio, Attica) as well as Mrs. Konstantina Kalafata and Dr. Ioannis Arabatzis for the kind supply of the nanocompounds used in this research work.

REFERENCES

- [1] Cassens, D.L. and Feist, W.C. "Exterior wood in the south: selection, application and finishes". USDA General Technical Report FPL-GTR-69, Madison, Wisconsin, USA, pp. 56, 1991.
- [2] Feist, W.C. and Hon, D.N.-S. "Chemistry of weathering and protection". Advances in Chemistry Series 207, pp. 401-457, 1984.
- [3] Fengel, D. and Wegener, G. "Wood: chemistry, ultrastructure, reactions". Walter de Gruyter, Berlin, New York, 1984.
- [4] Garcia, R.A., Lopes, J.O., do Nascimento, A.M., de Figueiredo Latorraca, J.V. "Color stability of weathered heat-treated teak wood". Maderas: Ciencia y Tecnología, 16 (2014): 4, 453-462.
- [5] Hon, D.N.-S. and Feist, W.C. "Free radicals formation in wood: The role of water". Wood Science 14 (1981): 41-48.
- [6] Hon, D.N.-S., G. Ifju, Feist, W.C. "Characterisation of free radicals in wood". Wood & Fiber Science, 12 (1980): 121-130.
- [7] Janin, G., Gonzales, J.C., Ananias, R., Charrier, B., Silva, G., Dilem, A. "Aesthetics appreciation of wood color and patterns by colorimetry: Part 1. Colorimetry theory for the CIELAB system". Maderas: Ciencia y Tecnología, 3 (2001): 3-13.
- [8] Kalnins, M.A. and Knaebe M.T. "Wettability of weathered wood". Journal of Adhesion Science and Technology, 6(12), (1992): 1325-1330.
- [9] Mc Donald, K.A., Falk, R.H., Williams, R.S., Winandy, J.E. "Wood decks, materials, construction and finishing". Forest Products Society, Madison, Wisconsin, USA, pp. 93, 1996.
- [10] Oltean, L., Németh, R., Hansmann, C., Teischinger, A. "Wood surface discoloration of three Hungarian hardwood species due to simulated indoor sunlight exposure". Wood Research, 55 (2010): 49-58.
- [11] Sahin, H.T., Mantanis, G.I. "Colour changes in wood surfaces modified by a nanoparticulate based treatment". Wood Research, 56(4): (2011a), 525-532.
- [12] Sahin, H.T., Mantanis, G.I. "Nano-based surface treatment effects on swelling, water sorption and hardness of wood". Maderas: Ciencia y Tecnología, 13(1): (2011b), 41-48.
- [13] Sandermann, W. and Schlumbom, F. "On the effect of filtered ultraviolet light on wood. Part II: kind and magnitude of colour difference on wood surfaces". Holz Roh- Werkstoff, 20 (1962): 285-291.
- [14] Tolvaj, L. and Mitsui, K. "Correlation between hue angle and lightness of light irradiated wood". Polymer Degradation and Stability, 95:4, (2010), 638-642.
- [15] Yamamoto, K., Kataoka, Y., Furuyama, Y., Matsuura, T., Kiguchi, M. "The effect of irradiation wavelength on the discoloration of wood". Mokuzai Gakkaishi, 53(6): (2007), 320-326.